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(54) Production of 2-hydrocarbyl-2-adamantyl acrylate compounds

Herstellung von 2-Hydrocarbyl-2-Adamantylacrylaten

Préparation d'acrylates de 2-hydrocarbyle-2-adamantyle

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(56) References cited:
EP-A- 1 020 767 **JP-A- 2000 229 911**

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a process for producing a 2-hydrocarbyl-2-adamantyl acrylate compound which gains industrial attention as a material for ArF excimer laser resists and high performance polymers.

2. Description of the Prior Art

[0002] In the known production of a 2-alkyl-2-adamantyl (meth)acrylate compound from a 2-adamantanone compound corresponding to its ester moiety, the 2-adamantanone compound is converted into a corresponding 2-alkyl-2-adamantanol compound, and then the 2-alkyl-2-adamantanol compound is reacted with (meth)acrylic acid or a (meth)acryloyl halide

[0003] K.Nozaki et al., Jpn. J. Appl. Phys., 35,528(1996) and EP1020767 report to synthesize 2-methyl-2-adamantyl methacrylate by the esterification reaction between 2-methyl-2-adamantanol and methacryloyl chloride. Japanese Patent Application Laid-Open No. 2000-229911 propose to synthesize a 2-alkyl-2-adamantyl (meth)acrylate by the reaction of a corresponding 2-alkyl-2-adamantanol compound with (meth)acryloyl chloride. Japanese Patent Application Laid-Open No. 2000-309558 discloses a reaction of a corresponding 2-alkyl-2-adamantanol compound or its metal salt with a (meth)acryloyl halide.

[0004] Japanese Patent Application Laid-Open No. 10-182552 discloses a process for producing an ester of tertiary alcohol without separating and purifying a tertiary alcohol, in which a starting ketone compound is reacted with a carboxylic acid halide in the presence of an organometallic compound to directly obtain the ester of tertiary alcohol. However, a (meth)acryloyl halide used as the esterification reagent is expensive and intractable, and contains various by-products which are difficult to remove. In addition, the (meth)acryloyl halide by-produces an alkyladamantyl halide which generates acid during distillation to decompose the target 2-alkyl-2-adamantyl (meth)acrylate compound, thereby significantly reducing the yield.

[0005] Japanese Patent Application Laid-Open No. 2000-97924 proposes to convert the alkyladamantyl halide to a compound which does not generate acid during distillation by contacting a 2-alkyl-2-adamantyl (meth)acrylate compound containing the alkyladamantyl halide with an alkali compound, thereby preventing the yield from being lowered. Japanese Patent Application Laid-Open No. 2000-229911 proposes a method for producing the 2-alkyl-2-adamantyl (meth)acrylate compound in high yields by using an acid halide prepared by reacting (meth)acrylic acid with benzoyl chloride or phosphorus trichloride.

[0006] However, since a production method using an acid halide should be carried out in a specific manner, it has been demanded to develop a production method which is easily operated in industrial scale and produces a 2-hydrocarbyl-2-adamantyl acrylate compound with high yields without using acid halide.

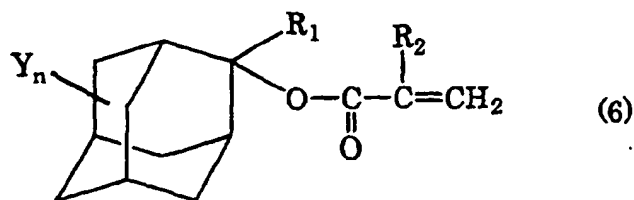
SUMMARY OF THE INVENTION

[0007] An object of the present invention is to provide a process for producing a 2-hydrocarbyl-2-adamantyl acrylate compound easily and stably with high yields from a 2-adamantanone compound without using a (meth)acryloyl halide.

[0008] As a result of extensive study in view of attaining the above object, the inventors have found that the 2-hydrocarbyl-2-adamantyl acrylate compound is efficiently produced from a 2-adamantanone compound by using a (meth)acrylic ester and/or an acrylic anhydride compound in place of the (meth)acryloyl halide. On the basis of this finding, the present invention has been accomplished.

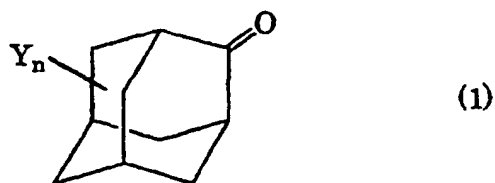
[0009] Thus, the present invention provides a process for producing a 2-hydrocarbyl-2-adamantyl acrylate compound represented by the following

Formula 6:



wherein R^1 is a hydrocarbyl group, R^2 is a hydrogen atom or an alkyl group, and Y is a hydrogen atom, an alkyl group, a hydroxyl group, or a halogen atom, and n is an integer of 1 to 14;

the process comprising a step of reacting a 2-adamantanone compound represented by the following Formula 1:



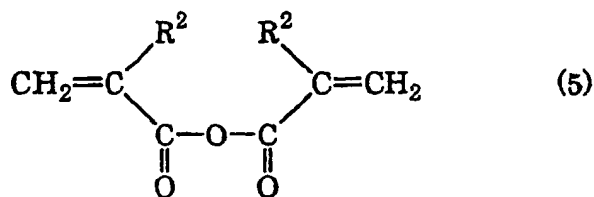
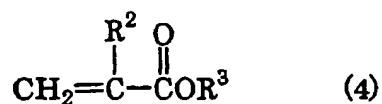
25 wherein Y and n are the same as defined above;

with at least one organometallic compound and at least one acrylic compound, the organometallic compound being represented by the following Formula 2 or 3:



35 wherein R^1 is the same as defined above, and X is a halogen atom;

and the acrylic compound being represented by the following Formula 4 or 5:

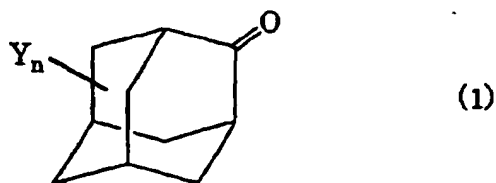


wherein R^2 is the same as defined above, and R^3 is an alkyl group.

55 DETAILED DESCRIPTION OF THE INVENTION

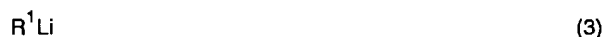
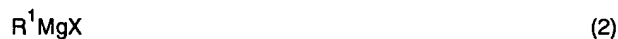
[0010] The 2-adamantanone compound (2-adamantanone and its derivatives) used as a starting material is repre-

sented by the following Formula 1:



[0011] In Formula 1, Y is a hydrogen atom, an alkyl group, a hydroxyl group, or a halogen atom. The alkyl group is preferably a C1-C10 alkyl such as methyl group, ethyl group, isopropyl group and amyl group. Examples of halogen atom is chlorine atom, bromine atom and iodine atom. The suffix "n" is an integer of 1 to 14, preferably 1 to 4. If n is 2 or more, two or more Y substituents may be the same as or different from each other. Particularly preferred 2-adamantanone compound is 2-adamantanone.

[0012] In the process of the present invention, a Grignard reagent represented by Formula 2 and/or an organolithium compound represented by Formula 3 is used as the organometallic compound.

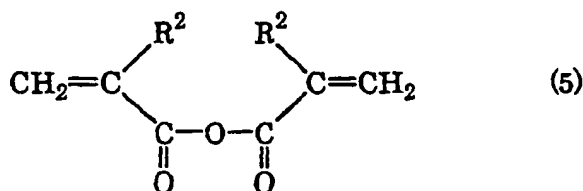
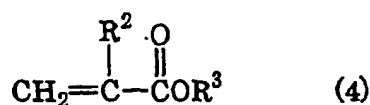


[0013] In Formulas 2 and 3, R¹ is a hydrocarbyl group, preferably an aliphatic, alicyclic or aromatic hydrocarbyl group having 1 to 10 carbon atoms, more preferably methyl group, ethyl group, propyl group, butyl group or phenyl group. X is a halogen such as chlorine, bromine and iodine. Specific Grignard reagent may be CH₃MgBr, C₂H₅MgBr, or C₄H₉MgBr, and a specific organolithium compound may be CH₃Li, C₂H₅Li or C₄H₉Li.

[0014] The Grignard reagent and the organolithium compound is added to the reaction system in the form of solution. As the solvent, usable are ether compounds such as tetrahydrofuran and diethyl ether; hydrocarbon compounds such as hexane, heptane and cyclohexane; and halogen compounds such as carbon tetrachloride and dichloromethane, although not limited thereto and another solvent is usable as far as inert to the reaction.

[0015] The Grignard reagent or the organolithium compound is used in an amount of 1 to 10 equivalents, preferably 1 to 2 equivalents based on the starting 2-adamantanone compound. Although the Grignard reagent or the organolithium compound may be added to the reaction system in any manner and at any addition speed, but preferably added at a speed so as to avoid the abnormal rise of the reaction temperature.

[0016] In the process of the present invention, the acrylic ester compound represented by the following Formula 4 and/or the acrylic anhydride compound represented by the following Formula 5 is used as the acrylic compound:



[0017] In Formulas 4 and 5, R² is a hydrogen atom or an alkyl group. The alkyl group is preferably a C1-C4 alkyl group such as methyl group and ethyl group. Preferred R² is a hydrogen atom or methyl group. R³ is an alkyl group,

preferably a C1-C6 alkyl group such as methyl group and ethyl group. The specific acrylic compound of Formula 4 is methyl ester, ethyl ester or isopropyl ester of acrylic acid or methacrylic acid; and the specific acrylic anhydride compound of Formula 5 is acrylic anhydride or methacrylic anhydride.

[0018] The addition amount of the acrylic compound is 1 to 100 equivalents, preferably 1 to 20 equivalents, more preferably 1 to 5 equivalents based on the starting 2-adamantanone compound. If less than one equivalent, the yield of the 2-hydrocarbyl-2-adamantyl acrylate compound is reduced. If more than 100 equivalents, the batch efficiency is lowered and the purification of the product becomes difficult.

[0019] The acrylic compound is added to the reaction system in any manner and in any addition speed. For example, the acrylic compound may be added to the reaction system prior to the addition of the Grignard reagent and/or the organolithium compound. Alternatively, the acrylic compound may be added simultaneously with the Grignard reagent and/or the organolithium compound. Preferably, the acrylic compound is added after the addition of the Grignard reagent and/or the organolithium compound.

[0020] The reaction temperature is -70 to 200°C, preferably -50 to 100°C. If the reaction temperature is lower than -70°C, the reaction rate is low. If higher than 200°C, the control of the reaction becomes difficult or the side reaction occurs to reduce the yield. The reaction temperature at the addition of the Grignard reagent and/or the organolithium compound and thereafter, and the reaction temperature at the addition of the acrylic ester compound and/or the acrylic anhydride compound and thereafter may be the same or different, and each reaction temperature may be varied by heating and cooling within the range of -70 to 200°C.

[0021] The reaction time for esterification is 0.5 to 1000 h, preferably 1 to 100 h, although not limited thereto because the reaction time depends on the reaction temperature and is determined according to the desired yield and another process factor.

[0022] R¹ of Formula 6 representing the 2-hydrocarbyl-2-adamantyl acrylate corresponds to R¹ of the Grignard reagent of Formula 2 and R¹ of the organolithium compound of Formula 3, and R² of Formula 6 corresponds to R² of the acrylic ester compound of Formula 4 and R² of the acrylic anhydride compound of Formula 5.

[0023] Although the objective 2-hydrocarbyl-2-adamantyl acrylate compound is produced in sufficiently high yields under reaction conditions mentioned above, the yield can be further enhanced by carrying out the reaction in the presence of an amine compound when the acrylic anhydride compound is used as the acrylic compound. Examples of the amine compound include methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, n-propylamine, di-n-propylamine, di-isopropylamine, tri-n-propylamine, n-butylamine, di-n-butylamine, di-isobutylamine, tri-n-butylamine, diphenylamine, 1,5-diazabicyclo[4.3.0]nonene-5, 1,5-diazabicyclo[5.4.0]undecene-5, and diazabicyclo[2.2.2]octane, with triethylamine being particularly preferred.

[0024] The reaction may be carried out, in addition to the amine compound, in the further presence of an aniline compound such as aniline, methylaniline, dimethylaniline, toluidine, anisidine, chloroaniline, bromoaniline, nitroaniline, and aminobenzoic acid; a nitrogen-containing heterocyclic compound such as a pyridine compound, a pyrrole compound, a quinoline compound, and a piperidine compound; a metal alkoxide such as sodium methoxide and lithium methoxide; a quaternary ammonium hydroxide such as tetramethylammonium hydroxide and trimethyl-n-propylammonium hydroxide; a sulfate, nitrate or hydrochloride of amine such as ethylammonium sulfate, trimethylammonium nitrate and anilinium chloride; or an inorganic base such as sodium hydrogencarbonate.

[0025] The addition amount of the amine compound is up to 100 equivalents excluding zero, preferably 0.000001 to 10 equivalents, more preferably 0.01 to 2 equivalents based on the starting 2-adamantanone compound. The use of the amine compound exceeding the above range creates no additional effect of enhancing the yield.

[0026] The manner for addition and the addition speed of the amine compound is not particularly limited. For example, the amine compound may be added to the reaction system prior to the addition of the organometallic compound (Grignard reagent and organolithium compound). Alternatively, the amine compound may be added to the reaction system after the addition of the organometallic compound, and before, simultaneously with or after the addition of the acrylic anhydride compound.

[0027] After completing the reaction, the reaction liquid is washed with water to remove the magnesium salt or the lithium salt derived from the Grignard reagent or the organolithium compound. The washing water may contain an appropriate inorganic salt such as sodium chloride and sodium hydrogencarbonate. The remaining non-reacted acrylic anhydride compound is removed by alkali washing using, but not limited thereto, an aqueous sodium hydroxide solution, an aqueous potassium hydroxide solution or an ammonia water. The metal impurities in the reaction liquid may be removed by acid washing using an aqueous solution of an inorganic acid such as hydrochloric acid, sulfuric acid and phosphoric acid or an aqueous solution of an organic acid such as oxalic acid. Since the remaining hydrochloric acid, even in a trace amount, decomposes the target compound during the distillation operation, it is preferred to use the inorganic acid other than hydrochloric acid.

[0028] An organic solvent may be added to the reaction liquid prior to the washing, if desired, in view of the properties of the produced 2-hydrocarbyl-2-adamantyl acrylate compound. The solvent to be added is the same as or different from the solvent used in the reaction. Usually, a low polar solvent which is easily separable from water is preferably

used. The 2-hydrocarbyl-2-adamantyl acrylate compound is separated from the organic layer by a known method such as distillation, concentration, filtration, crystallization, recrystallization and column chromatography.

[0029] The present invention will be described in more detail by way of the following examples. However, it should be noted that the following examples are not intended to limit the scope of the present invention thereto.

EXAMPLE 1

[0030] Into a 3-necked flask, were charged 5.0 g of 2-adamantanone and 50 mL of tetrahydrofuran (THF), and the contents were cooled to -25°C by ethylene glycol/water under nitrogen atmosphere. Then, 35 mL of an ether solution of methyl lithium (1.2 equivalents based on 2-adamantanone) was slowly added dropwise to the flask while keeping the contents of the flask at -25 to -20°C. After completing the dropwise addition, the stirring was further continued for additional one hour. Then, 10 g of methyl methacrylate (3 equivalents based on 2-adamantanone) was slowly added dropwise. After the addition, the reaction was allowed to proceed at 55°C for 4.5 h by immersing the flask into a silicone bath.

[0031] After completing the reaction, 25 mL of hexane and 25 mL of a saturated aqueous sodium chloride were added to the reaction liquid, and the mixture was stirred sufficiently. After causing the mixture to liquid-liquid separation, the organic layer was washed twice with 20 mL aliquot of pure water, and concentrated to remove the solvent and the non-reacted methyl methacrylate, thereby obtaining a crude product. By purifying the crude product through a silica-gel column, 7.4 g (96% yield), as determined by GC-MS analysis and ¹H NMR analysis, of pure 2-methyl-2-adamantyl methacrylate was obtained.

EXAMPLE 2

[0032] Into a 3-necked flask, were charged 5.0 g of 2-adamantanone and 50 mL of tetrahydrofuran (THF), and the contents were cooled to -25°C by ethylene glycol/water under nitrogen atmosphere. Then, 13 mL of an ether solution of methyl magnesium bromide (1.2 equivalents based on 2-adamantanone) was slowly added dropwise to the flask while keeping the contents of the flask at -25 to -20°C. After completing the dropwise addition, the stirring was further continued for additional one hour. Then, 10 g of methyl methacrylate (3 equivalents based on 2-adamantanone) was slowly added dropwise. After the addition, the reaction was allowed to proceed at 60°C for 6 h by immersing the flask into a silicone bath.

[0033] After completing the reaction, 25 mL of hexane and 25 mL of a saturated aqueous sodium chloride were added to the reaction liquid, and the mixture was stirred sufficiently. After causing the mixture to liquid-liquid separation, the organic layer was washed twice with 20 mL aliquot of pure water, and concentrated to remove the solvent and the non-reacted methyl methacrylate, thereby obtaining a crude product. By purifying the crude product through a silica-gel column, 6.9 g (88% yield) of pure 2-methyl-2-adamantyl methacrylate was obtained.

EXAMPLE 3

[0034] Into a 3-necked flask, were charged 5.0 g of 2-adamantanone and 50 mL of tetrahydrofuran (THF), and the contents were cooled to -25°C by ethylene glycol/water under nitrogen atmosphere. Then, 35 mL of an ether solution of methyl lithium (1.2 equivalents based on 2-adamantanone) was slowly added dropwise to the flask while keeping the contents of the flask at -25 to -20°C. After completing the dropwise addition, the stirring was further continued for additional one hour. Then, 10 g of methacrylic anhydride (2 equivalents based on 2-adamantanone) was slowly added dropwise. After the addition, the reaction was allowed to proceed at 55°C for 3 h by immersing the flask into a silicone bath.

[0035] After completing the reaction, 25 mL of hexane and 25 mL of a saturated aqueous sodium chloride were added to the reaction liquid, and the mixture was stirred sufficiently. After causing the mixture to liquid-liquid separation, the organic layer was added with 20 mL of a 5% aqueous solution of sodium hydroxide and then stirred sufficiently to remove the non-reacted methacrylic anhydride. The organic layer was washed twice with 20 mL aliquot of pure water, and concentrated to remove the solvent, thereby obtaining a crude product. By purifying the crude product through a silica-gel column, 7.1 g (90% yield) of pure 2-methyl-2-adamantyl methacrylate was obtained.

EXAMPLE 4

[0036] Into a 3-necked flask, were charged 5.0 g of 2-adamantanone and 50 mL of tetrahydrofuran (THF), and the contents were cooled to -25°C by ethylene glycol/water under nitrogen atmosphere. Then, 13 mL of an ether solution of methyl magnesium bromide (1.2 equivalents based on 2-adamantanone) was slowly added dropwise to the flask while keeping the contents of the flask at -25 to -20°C. After completing the dropwise addition, the stirring was further

continued for additional one hour. Then, 10 g of methacrylic anhydride (2 equivalents based on 2-adamantanone) was slowly added dropwise. After the addition, the reaction was allowed to proceed at 55°C for 3 h by immersing the flask into a silicone bath.

[0037] After completing the reaction, 25 mL of hexane and 25 mL of a saturated aqueous sodium chloride were added to the reaction liquid, and the mixture was stirred sufficiently. After causing the mixture to liquid-liquid separation, the organic layer was added with 20 mL of a 5% aqueous solution of sodium hydroxide and then stirred sufficiently to remove the non-reacted methacrylic anhydride. The organic layer was washed twice with 20 mL aliquot of pure water, and concentrated to remove the solvent, thereby obtaining a crude product. By purifying the crude product through a silica-gel column, 6.6 g (85% yield) of pure 2-methyl-2-adamantyl methacrylate was obtained.

EXAMPLE 5

[0038] Into a 3-necked flask, were charged 5.0 g of 2-adamantanone and 50 mL of tetrahydrofuran (THF), and the contents were cooled to -25°C by ethylene glycol/water under nitrogen atmosphere. Then, 35 mL of an ether solution of methyl lithium (1.2 equivalents based on 2-adamantanone) was slowly added dropwise to the flask while keeping the contents of the flask at -25 to -20°C. After completing the dropwise addition, the stirring was further continued for additional one hour. Then, 0.4 g of triethylamine (0.1 equivalent based on 2-adamantanone) and 7.7 g of methacrylic anhydride (1.5 equivalents based on 2-adamantanone) were successively and slowly added dropwise. After the addition, the reaction was allowed to proceed at 25°C for 1.5 h by immersing the flask into a silicone bath.

[0039] After completing the reaction, 25 mL of hexane and 25 mL of a saturated aqueous sodium chloride were added to the reaction liquid, and the mixture was stirred sufficiently. After causing the mixture to liquid-liquid separation, the organic layer was added with 20 mL of a 5% aqueous solution of sodium hydroxide and then stirred sufficiently to remove the non-reacted methacrylic anhydride. The organic layer was washed twice with 20 mL aliquot of pure water, and concentrated to remove the solvent, thereby obtaining a crude product. By purifying the crude product through a silica-gel column, 7.6 g (97% yield) of pure 2-methyl-2-adamantyl methacrylate was obtained when determined by GC-MS analysis and ¹H NMR analysis.

EXAMPLE 6

[0040] Into a 3-necked flask, were charged 5.0 g of 2-adamantanone and 50 mL of tetrahydrofuran (THF), and the contents were cooled to -25°C by ethylene glycol/water under nitrogen atmosphere. Then, 38 mL of an ether solution of methyl magnesium bromide (1.05 equivalents based on 2-adamantanone) was slowly added dropwise to the flask while keeping the contents of the flask at -25 to -10°C. After completing the dropwise addition, the stirring was further continued for additional one hour. Then, 1.21 g of triethylamine (0.3 equivalent based on 2-adamantanone) and 7.7 g of methacrylic anhydride (1.5 equivalents based on 2-adamantanone) were successively and slowly added dropwise. After the addition, the reaction was allowed to proceed at 25°C for 1.5 h by immersing the flask into a silicone bath.

[0041] After completing the reaction, 25 mL of hexane and 25 mL of a saturated aqueous sodium chloride were added to the reaction liquid, and the mixture was stirred sufficiently. After causing the mixture to liquid-liquid separation, the organic layer was added with 20 mL of a 5% aqueous solution of sodium hydroxide and then stirred sufficiently to remove the non-reacted methacrylic anhydride. The organic layer was washed twice with 20 mL aliquot of pure water, and concentrated to remove the solvent, thereby obtaining a crude product. By purifying the crude product through a silica-gel column, 7.4 g (95% yield) of pure 2-methyl-2-adamantyl methacrylate was obtained.

EXAMPLE 7

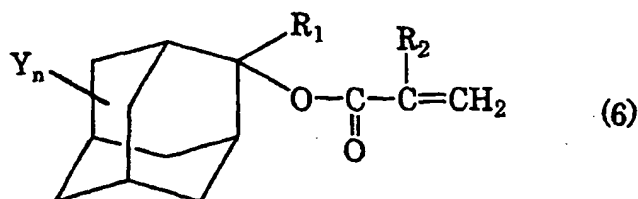
[0042] Into a 3-necked flask, were charged 50 g of 2-adamantanone and 500 mL of tetrahydrofuran (THF), and the contents were cooled to -25°C by ethylene glycol/water under nitrogen atmosphere. Then, 130 mL of an ether solution of methyl magnesium bromide (1.05 equivalents based on 2-adamantanone) was slowly added dropwise to the flask while keeping the contents of the flask at -25 to -20°C. After completing the dropwise addition, the stirring was further continued for additional one hour. Then, 77 g of methacrylic anhydride (1.5 equivalents based on 2-adamantanone) and 12 g of triethylamine (0.3 equivalent based on 2-adamantanone) were simultaneously and slowly added dropwise. After the addition, the reaction was allowed to proceed at 25°C for 1.5 h by immersing the flask into a silicone bath.

[0043] After completing the reaction, 250 mL of hexane and 250 mL of a saturated aqueous sodium chloride were added to the reaction liquid, and the mixture was stirred sufficiently. After causing the mixture to liquid-liquid separation, the organic layer was added with 200 mL of a 5% aqueous solution of sodium hydroxide and then stirred sufficiently to remove the non-reacted methacrylic anhydride. The organic layer was washed twice with 200 mL aliquot of pure water, and concentrated to remove the solvent, thereby obtaining 80 g of a crude product. By purifying the crude product by distillation, 72 g (92% yield) of 2-methyl-2-adamantyl methacrylate (98% purity) was obtained.

[0044] According to the present invention, since the esterification reaction proceeds nearly quantitatively, a highly pure 2-hydrocarbyl-2-adamantyl acrylate compound is obtained in high yields by a simple purification. In addition, the process can be simplified because steps of separation and purification of an intermediate 2-hydrocarbyl-2-adamantanol compound are not needed.

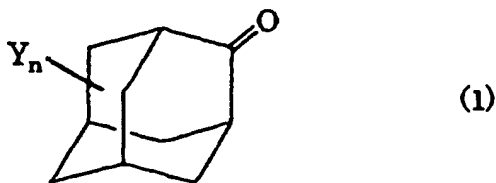
Claims

1. A process for producing a 2-hydrocarbyl-2-adamantyl acrylate compound represented by the following Formula 6:



wherein R¹ is a hydrocarbyl group, R² is a hydrogen atom or an alkyl group, Y is a hydrogen atom, an alkyl group, a hydroxyl group or a halogen atom, and n is an integer of 1 to 14;

the process comprising a step of reacting a 2-adamantanone compound represented by the following Formula 1:



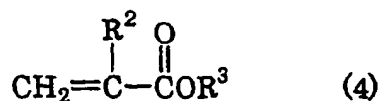
wherein Y and n are the same as defined above;

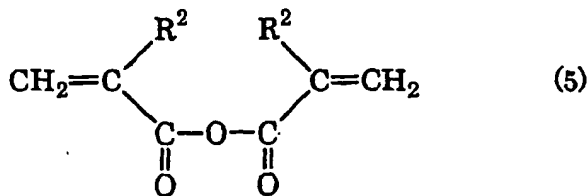
with at least one organometallic compound and at least one acrylic compound, the organometallic compound being represented by the following Formula 2 or 3:



wherein R¹ is the same as defined above, and X is a halogen atom;

and the acrylic compound being represented by the following Formula 4 or 5:





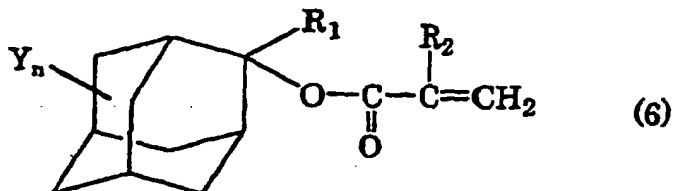
wherein R² is the same as defined above, and R³ is an alkyl group.

2. The process according to claim 1, wherein Y of Formula 1 or 6 is a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a hydroxyl group, or a halogen atom.
3. The process according to claim 2, the alkyl group is methyl group, ethyl group, isopropyl group, or amyl group.
4. The process according to claim 1 or 2, wherein the 2-adamantanone compound of Formula 1 is 2-adamantanone.
5. The process according to any one of claims 1 to 4, wherein R¹ of Formula 2 or 3 is an aliphatic, alicyclic or aromatic hydrocarbonyl group having 1 to 10 carbon atoms.
6. The process according to claim 5, wherein R¹ is methyl group, ethyl group, propyl group, butyl group, or phenyl group.
7. The process according to any one of claims 1 to 6, wherein the organometallic compound of Formula 2 is CH₃MgBr, C₂H₅MgBr, or C₄H₉MgBr.
8. The process according to any one of claims 1 to 6, wherein the organometallic compound of Formula 3 is CH₃Li, C₂H₅Li, or C₄H₉Li.
9. The process according to any one of claims 1 to 8, wherein the organometallic compound of Formula 2 and/or 3 is used in an amount of 1 to 10 equivalents based on the 2-adamantanone compound of Formula 1.
10. The process according to any one of claims 1 to 9, wherein R² of Formula 4 or 5 is a hydrogen atom or an alkyl group having 1 to 4 carbon atom.
11. The process according to claim 10, wherein R² is a hydrogen atom or methyl group.
12. The process according to any one of claims 1 to 11, wherein R³ of Formula 4 is an alkyl group having 1 to 6 carbon atoms.
13. The process according to any one of claims 1 to 12, wherein the acrylic compound of Formula 4 is methyl acrylate, ethyl acrylate, isopropyl acrylate, methyl methacrylate, ethyl methacrylate, or isopropyl methacrylate.
14. The process according to any one of claims 1 to 12, wherein the acrylic compound of Formula 5 is acrylic anhydride or methacrylic anhydride.
15. The process according to any one of claims 1 to 14, wherein the acrylic compound of Formula 4 and/or 5 is used in an amount of 1 to 100 equivalents based on the 2-adamantanone compound.
16. The process according to any one of claims 1 to 15, wherein the 2-adamantanone compound of Formula 1 is reacted with the organometallic compound of Formula 2 and/or 3 and the acrylic ester compound of Formula 4 and/or 5 at -70 to 200 °C.
17. The process according to any one of claims 1 to 11 and 14 to 16, wherein the 2-adamantanone compound of Formula 1 is reacted with at least one of the organometallic compounds of Formulas 2 and 3 and the acrylic anhydride compound of Formula 5 in the presence of an amine compound.

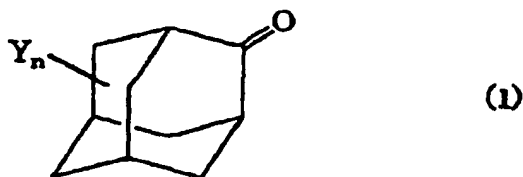
18. The process according to claim 17, wherein the amine compound is at least one compound selected from the group consisting of methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, n-propylamine, di-n-propylamine, di-isopropylamine, tri-n-propylamine, n-butylamine, di-n-butylamine, di-isobutylamine, tri-n-butylamine, diphenylamine, 1,5-diazabicyclo[4.3.0]nonene-5, 1,5-diazabicyclo[5.4.0]undecene-5, and diazabicyclo[2.2.2]octane.

Patentansprüche

1. Verfahren zur Herstellung einer durch die folgende Formel 6 dargestellten 2-Hydrocarbyl-2-adamantyl-acrylat-Verbindung:



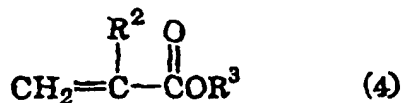
wobei R¹ eine Hydrocarbylgruppe ist, R² ein Wasserstoffatom oder eine Alkylgruppe ist; Y ein Wasserstoffatom, eine Alkylgruppe, eine Hydroxylgruppe oder ein Halogenatom ist; und n eine ganze Zahl von 1 bis 14 ist; wobei das Verfahren einen Schritt der Umsetzung einer durch die folgende Formel 1 dargestellten 2-Adamantanon-Verbindung:

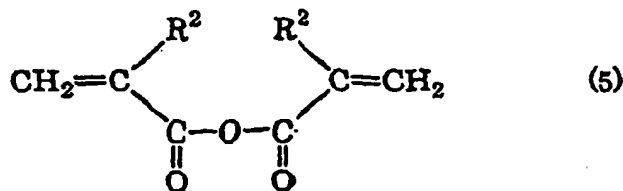


wobei Y und n wie oben definiert sind; mit mindestens einer organometallischen Verbindung und mindestens einer Acryl-Verbindung umfasst, wobei die organometallische Verbindung durch die folgende Formel 2 oder 3 dargestellt wird:



wobei R¹ wie oben definiert ist, und Y ein Halogenatom ist; und die Acryl-Verbindung durch die folgenden Formeln 4 oder 5 dargestellt wird:





wobei R^2 wie oben definiert ist, und R^3 eine Alkylgruppe ist.

2. Verfahren nach Anspruch 1, wobei Y in Formel 1 oder 6 ein Wasserstoff, eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen, eine Hydroxylgruppe oder ein Halogenatom ist.

3. Verfahren nach Anspruch 2, wobei die Alkylgruppe eine Methylgruppe, Ethylgruppe, Isopropylgruppe oder Amylgruppe ist.

4. Verfahren nach Anspruch 1 oder 2, wobei die 2-Adamantanon-Verbindung der Formel 1 2-Adamantanon ist.

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei R^1 der Formel 2 oder 3 eine aliphatische, alicyclische oder aromatische Hydrocarbylgruppe mit 1 bis 10 Kohlenstoffatomen ist.

6. Verfahren nach Anspruch 5, wobei R^1 eine Methylgruppe, Ethylgruppe, Propylgruppe, Butylgruppe oder Phenylgruppe ist.

7. Verfahren nach einem der Ansprüche 1 bis 6, wobei die organometallische Verbindung der Formel 2 CH_3MgBr , $\text{C}_2\text{H}_5\text{MgBr}$ oder $\text{C}_4\text{H}_9\text{MgBr}$ ist.

8. Verfahren nach einem der Ansprüche 1 bis 6, wobei die organometallische Verbindung der Formel 3 CH_3Li , $\text{C}_2\text{H}_5\text{Li}$ oder $\text{C}_4\text{H}_9\text{Li}$ ist.

9. Verfahren nach einem der Ansprüche 1 bis 8, wobei die organometallische Verbindung der Formel 2 und/oder 3 in einer Menge von 1 bis 10 Äquivalenten bezogen auf die 2-Adamantanon-Verbindung der Formel 1 verwendet wird.

10. Verfahren nach einem der Ansprüche 1 bis 9, wobei R^2 der Formel 4 oder 5 ein Wasserstoffatom oder eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen ist.

11. Verfahren nach Anspruch 10, wobei R^2 ein Wasserstoffatom oder eine Methylgruppe ist.

12. Verfahren nach einem der Ansprüche 1 bis 11, wobei R^3 der Formel 4 eine Alkylgruppe mit 1 bis 6 Kohlenstoffatomen ist.

13. Verfahren nach einem der Ansprüche 1 bis 12, wobei die Acryl-Verbindung der Formel 4 Methylacrylat, Ethylacrylat, Isopropylacrylat, Methylmethacrylat, Ethylmethacrylat oder Isopropylmethacrylat ist.

14. Verfahren nach einem der Ansprüche 1 bis 12, wobei die Acryl-Verbindung der Formel 5 Acrylsäureanhydrid oder Methacrylsäureanhydrid ist.

15. Verfahren nach einem der Ansprüche 1 bis 14, wobei die Acryl-Verbindung der Formel 4 und/oder 5 in einer Menge von 1 bis 100 Äquivalenten bezogen auf die 2-Adamantanon-Verbindung eingesetzt wird.

16. Verfahren nach einem der Ansprüche 1 bis 15, wobei die 2-Adamantanon-Verbindung der Formel 1 mit der organometallischen Verbindung der Formel 2 und/oder 3 und der Acrylester-Verbindung der Formel 4 und/oder 5 bei -70 bis 200°C umgesetzt wird.

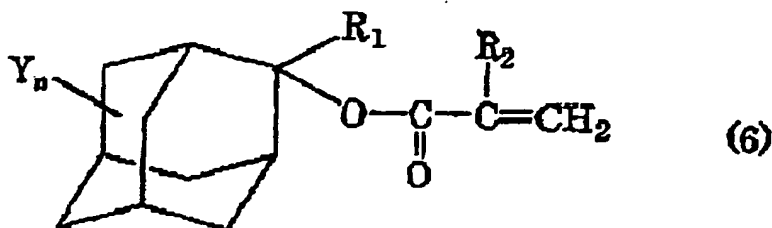
17. Verfahren nach einem der Ansprüche 1 bis 11 und 14 bis 16, wobei die 2-Adamantanon-Verbindung der Formel 1 mit mindestens einer der organometallischen Verbindungen der Formeln 2 und 3 und der Acrylsäureanhydrid-

Verbindung der Formel 5 in Gegenwart einer Amin-Verbindung umgesetzt wird.

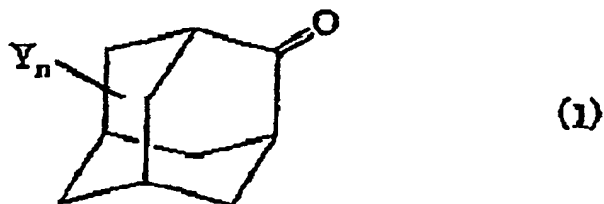
18. Verfahren nach Anspruch 17, wobei die Amin-Verbindung mindestens eine Verbindung ist, die ausgewählt wird aus der aus Methylamin, Dimethylamin, Trimethylamin, Ethylamin, Diethylamin, Triethylamin, n-Propylamin, Di-n-propylamin, Di-isopropylamin, Tri-n-propylamin, n-Butylamin, Di-n-butylamin, Di-isobutylamin, Tri-n-butylamin, Diphenylamin, 1,5-Diazabicyclo[4.3.0]nonen-5, 1,5-Diazabicyclo[5.4.0]undecen-5 und Diazabicyclo[2.2.2]octan bestehenden Gruppe.

Revendications

1. Procédé de production d'un composé d'acrylate de 2-hydrocarbyl-2-adamantyle représenté par la formule 6 suivante :



dans laquelle R^1 est un groupe hydrocarbyle, R^2 est un atome d'hydrogène ou un groupe alkyle, Y est un atome d'hydrogène, un groupe alkyle, un groupe hydroxyle ou un atome d'halogène, et n est un entier de 1 à 14 ;
le procédé comprenant une étape de mise en réaction d'un composé de 2-adamantanone représenté par la formule 1 suivante :

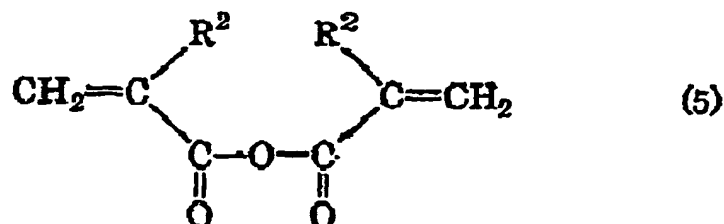


dans laquelle Y et n sont tels que définis précédemment ;
avec au moins un composé organométallique et au moins un composé d'acrylique, le composé organométallique étant représenté par la formule 2 ou 3 suivante :



dans lesquelles R^1 est tel que défini précédemment, et X est un atome d'halogène ;
et le composé d'acrylique étant représenté par la formule 4 ou 5 suivante :





dans lesquelles R^2 est tel que défini précédemment, et R^3 est un groupe alkyle.

2. Procédé selon la revendication 1, dans lequel Y de la formule 1 ou 6 est un atome d'hydrogène, un groupe alkyle ayant 1 à 10 atomes de carbone, un groupe hydroxyle, ou un atome d'halogène.
3. Procédé selon la revendication 2, dans lequel le groupe alkyle est un groupe méthyle, un groupe éthyle, un groupe isopropyle, ou un groupe amyle.
4. Procédé selon la revendication 1 ou 2, dans lequel le composé de 2-adamantanone de formule 1 est la 2-adamantanone.
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel R¹ de la formule 2 ou 3 est un groupe aliphatique, alicyclique ou aromatique ayant 1 à 10 atomes de carbone.
6. Procédé selon la revendication 5, dans lequel R¹ est un groupe méthyle, un groupe éthyle, un groupe propyle, un groupe butyle, ou un groupe phényle.
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel le composé organométallique de formule 2 est CH₃MgBr, C₂H₅MgBr, ou C₄H₉MgBr.
8. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel le composé organométallique de formule 3 est CH₃Li, C₂H₅Li, ou C₄H₉Li.
9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel le composé organométallique de formule 2 et/ou 3 est utilisé dans une quantité de 1 à 10 équivalents par rapport au composé de 2-adamantanone de formule 1.
10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel R² de la formule 4 ou 5 est un atome d'hydrogène ou un groupe alkyle ayant 1 à 4 atomes de carbone.
11. Procédé selon la revendication 10, dans lequel R² est un atome d'hydrogène ou un groupe méthyle.
12. Procédé selon l'une quelconque des revendications 1 à 11, dans lequel R³ de la formule 4 est un groupe alkyle ayant 1 à 6 atomes de carbone.
13. Procédé selon l'une quelconque des revendications 1 à 12, dans lequel le composé d'acrylique de formule 4 est l'acrylate de méthyle, l'acrylate d'éthyle, l'acrylate d'isopropyle, le méthacrylate de méthyle, le méthacrylate d'éthyle, ou le méthacrylate d'isopropyle.
14. Procédé selon l'une quelconque des revendications 1 à 12, dans lequel le composé d'acrylique de formule 5 est l'anhydride acrylique ou l'anhydride méthacrylique.
15. Procédé selon l'une quelconque des revendications 1 à 14, dans lequel le composé d'acrylique de formule 4 et/ou 5 est utilisé dans une quantité de 1 à 100 équivalents par rapport au composé de 2-adamantanone.
16. Procédé selon l'une quelconque des revendications 1 à 15, dans lequel le composé de 2-adamantanone de formule 1 est mis à réagir avec le composé organométallique de formule 2 et/ou 3 et le composé d'ester acrylique de formule 4 et/ou 5 à une température de -70 à 200 °C.

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17. Procédé selon l'une quelconque des revendications 1 à 11 et 14 à 16, dans lequel le composé de 2-adamantanone de formule 1 est mis à réagir avec au moins un des composés organométalliques de formules 2 et 3 et le composé d'anhydride acrylique de formule 5 en présence d'un composé d'amine.

18. Procédé selon la revendication 17, dans lequel le composé d'amine est au moins un composé choisi dans le groupe constitué par la méthylamine, la diméthylamine, la triméthylamine, l'éthylamine, la diéthylamine, la triéthylamine, la n-propylamine, la di-n-propylamine, la di-isopropylamine, la tri-n-propylamine, la n-butylamine, la di-n-butylamine, la di-isobutylamine, la tri-n-butylamine, la diphénylamine, la 1,5-diazabicyclo[4.3.0]non-5-ène, la 1,5-diazabicyclo[5.4.0]undéc-5-ène, et la diazabicyclo[2.2.2]octane.